

Electrical characterization of a phenylacetylene-modified silicon surface via mercury probe

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 446003

(<http://iopscience.iop.org/0953-8984/19/44/446003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 06:29

Please note that [terms and conditions apply](#).

Electrical characterization of a phenylacetylene-modified silicon surface via mercury probe

R K Hiremath¹, B G Mulimani^{1,3}, M K Rabinal^{1,4} and I M Khazi²

¹ Department of Physics, Karnatak University, Dharwad 580003, India

² Department of Chemistry, Karnatak University, Dharwad 580003, India

E-mail: mkrabinal@yahoo.com

Received 13 June 2007, in final form 25 July 2007

Published 24 September 2007

Online at stacks.iop.org/JPhysCM/19/446003

Abstract

The influence of phenylacetylene molecules on a silicon (100) surface has been investigated by formation of metal–molecule–semiconductor junctions with soft mercury contacts. Molecules are bonded covalently to the semiconductor surface via Si–C bonds by thermochemical reaction. The chemical bonding of these molecules is confirmed by XPS measurements. Current–voltage and capacitance–voltage curves were recorded under dark and light on these junctions to understand the role of the organic molecules. Junctions with phenylacetylene molecules are more ideal, with an extra density of surface states which are responsible for quenching photoconductivity. The presence of surface states is reflected as well-defined peaks in low frequency photocapacitance curves.

1. Introduction

Tuning the surface states of semiconductors to explore their potential uses in modern electronic devices is progressing at a rapid rate [1–4]. Attempts are being made to control the surface states by either organic [5, 6] or inorganic routes of passivation [7, 8]. Organic passivation has proved to be the simplest and most effective method that allows precise control of surface states by anchoring organic molecules to semiconductor surfaces under ambient conditions. This method yields superior surfaces for use in modern electronic devices [9]. The bonded molecules play a pivotal role in communicating electronically with the energy bands of the semiconductor and contacting metal [10]. Organic molecules with terminally unsaturated hydrocarbons can bond covalently, via Si–C chemistry, on hydrated silicon surfaces. Such bonds are thermodynamically and kinetically stable due to their high bond strength and low

³ Present address: Gulbarga University, Gulbarga 585106, India.

⁴ Author to whom any correspondence should be addressed.

polarity [11]. Spectroscopically, these interfaces are well studied and found to be highly durable under adverse conditions [12–14]. In the literature, various methods have been adopted to form the covalent bonds of organic molecules to create uniform and densely packed monolayers on silicon surfaces. Some of these methods are photochemical, thermochemical, electrochemical, mechanochemical and hydrosilylation by Grignard reactions [15, 16].

Monolayers of π -conjugated organic molecules on semiconductors are of special interest as they have the ability to function as electrically active interfaces at the metal–molecule–semiconductor junctions [17]. They possess very promising optoelectronic properties such as anisotropic electrical conductivity, high charge mobility, electro-optical switching behavior etc [18, 19]. Phenylacetylene (PA) is a prototypical alkyne that has two chemically active sites: one is the acetylene triple bond and another is π -conjugation of benzene ring. As a result, this molecule can undergo different adsorption configurations depending on which of these sites takes part in chemical bonding with the surface atoms of silicon [20, 21]. If the adsorption occurs through the acetylene group then the rich π -conjugation of benzene may exhibit interesting optoelectronic properties and it can also be a good functional site for further attachment of organic molecules.

In this paper we present charge transport properties of organically modified silicon surfaces ($\text{Si:C}_8\text{H}_6$) by thermal attachment of PA molecules and H-terminated silicon surfaces (Si:H) using soft electrical contacts.

2. Experimental details

2.1. Starting materials

Commercial single crystals of silicon (p-type, (100)-orientation, $4 \Omega \text{ cm}$ and one-side mirror polished, supplied by the Semiconductor Wafer Inc., Taiwan) were chosen for the present work. The unpolished side of the sample was coated with aluminum film by thermal evaporation under a 1×10^{-6} Torr vacuum. It was then annealed under a similar vacuum at $700 \text{ }^\circ\text{C}$ for 10 min to obtain a reliable back ohmic contact. This served as the starting material for the rest of the device fabrication. PA (98%, Sigma-Aldrich) was used for the chemical bonding on the Si surface.

2.2. Monolayer preparation

The formation of well-ordered and stable monolayers on a silicon surface is a challenging task. The easiest and technologically most promising route is hydrosilylation of H-terminated silicon surfaces by unsaturated organic molecules; this has been successfully carried out on Si(100) surfaces [22]. Etching of silicon in HF removes native oxide over its surface and produces a uniform H-terminated surface, favorable for the attachment of organic molecules [23]. Thermal attachment of PA was carried out by hydrosilylation of the Si–H surface under dry nitrogen. An L-type Teflon set-up (80 mm long) with a smooth base (15 mm wide and 25 mm long) was specially designed for HF etching. A piece of Si ($5 \times 10 \text{ mm}^2$) with back ohmic contact was cut and degreased in hot trichloroethylene and placed on a Teflon base. Two to three drops of diluted HF was carefully spread over the silicon surface to cover the entire region. After 5 min, the solution was quickly and carefully sucked up with a piece of clean tissue paper without touching the surface. The base of the Teflon set-up along with the sample was immediately immersed in sufficient deionized water. The sample was rinsed and transferred to a long test tube containing $500 \mu\text{l}$ of PA solution. The portion of test tube containing the solution and sample was heated in a small metal block furnace (homemade) at a constant temperature of

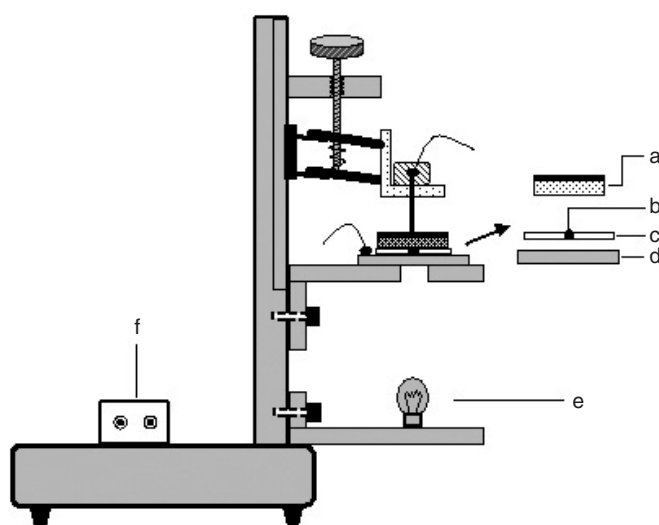


Figure 1. Experimental set-up for conductivity measurements with mercury as the soft electrical contact: (a) sample with back contact, (b) mercury drop, (c) thin film of PDMS, (d) ITO glass, (e) light source and (f) BNC connectors.

120 °C for 2 h under dry nitrogen. The resulting sample was thoroughly rinsed in mesitylene and then in ethanol, dried under nitrogen and loaded for conductivity measurements. It has been observed that during the hydrosilylation reaction, PA bonds to the silicon surface through acetylene groups only [24]. Therefore, in the present treatment, we assume this as the possible configuration.

2.3. Junction preparation and conductivity set-up

Molecularly modified surfaces require soft electrical contacts to measure the effect induced by the molecules [25]. This involves contacting individual/groups of molecules with minimum mechanical stress/damage. It is well reported that the stress and nature of the chemical bond between metal and molecules have profound effects on electrical charge transport through these junctions [26]. The simplest way to form contact is by thermal evaporation of metal on molecules; many times this runs with a risk of shorting of contacts [27, 28]. To overcome this problem, other methods like nanoscale junctions [29], lift-off float [30], scanning probes [31], soft contacts (mercury probe) [32], nano-transfer printing (nTP) and soft contact lamination (ScL) [33] have been proposed. Nano-transfer printing offers superior contacts between metal and molecules by covalent bonding, if the end moiety of molecule is a thiol linkage and contacting metal is gold [34]; it cannot be realized in many of the molecular junctions. On the other hand, for laboratory characterization, the soft contact (mercury drop) method is easy and simple to characterize chemically modified semiconductors before being implemented for their potential applications. In case of Si-based junctions mercury is the most suitable soft contact since it does not react with Si [35].

We report a simple homemade conductivity set-up that is shown in figure 1. It permits us to make reproducible and stable contacts to Si surfaces. It has two horizontal platforms fixed to a commercial set-up, used for four-probe conductivity measurements. The upper plate has a hole of 4 mm diameter at its center and a transparent electrode (indium tin oxide (ITO), with

sheet resistance $10 \Omega \text{ cm}^2$, supplied by Merck, Germany) is firmly glued over the hole such that the conducting face of ITO is upright. The lower platform is fixed at a distance of 10 cm, with a source of white light (halogen lamp, 20 W) positioned directly below the hole in the upper plate to facilitate photocurrent and photocapacitance measurements. Provision was also made to fix a high intensity blue LED close to the sample to conduct the photoconductivity measurements. A thin sheet of polydimethylsiloxane (PDMS) film (0.5 mm thick and with an area of 80 mm^2) with a central hole of 1.5 mm diameter is placed on ITO and a little drop of mercury (a known quantity every time) is injected into the PDMS hole. The wetting nature of PDMS with mercury helps to confine the mercury to the restricted volume. The sample with its chemically treated surface is placed in contact with the mercury, and a reproducible amount of pressure was applied on samples back through a tungsten tip loaded with spring-back, as shown in figure 1. This needle acts as a top electrode (in contact with back side of the silicon) and the conducting surface of the ITO in contact with mercury acts as a bottom electrode (contact to organic molecules); contact from ITO was further extended using silver paint. The junctions thus formed, on both untreated and chemically treated silicon surfaces, constitute mercury–silicon and mercury–molecule–silicon junctions. The two end contacts were extended to the BNC connectors for current–voltage (I – V) and capacitance–voltage (C – V) measurements. The I – V and C – V measurements were done with Keithley 617 and 6512 electrometers and an Agilent 4284A LCR meter. The PA modified silicon surface was immediately transferred to the conductivity set-up for electrical characterization soon after its preparation. Each I – V and C – V curve that is shown in various figures is an average over eight to ten sets of measurements.

X-ray photoelectron spectroscopy (XPS) and ellipsometric measurements were carried out to confirm the chemical bonding of PA molecules to the silicon surface. The thickness of the molecular film on the Si surface and that of the oxide layer on bare silicon was measured by ellipsometry (SENTECH SE850) at an incident angle of 60° with $\lambda = 670 \text{ nm}$ source. XPS measurements were done with a VG Scientific, ESCALAB MK-IV spectrometer with Al $K\alpha$ (1486.6 eV) at a take-off angle of 35° under a 5×10^{-8} Torr vacuum.

3. Results and discussion

3.1. Surface characterization

Figure 2 shows XPS spectra recorded under a high vacuum for bare (dashed line) and PA-treated Si (solid line) surfaces. Figure 2(a) reveals the Si(2p) peak at 99.6 eV, on both samples. A chemical shift due to the formation of SiO_2 at 103 eV is observed on bare Si (dashed line) and is absent on molecularly treated Si, indicating that the latter is free from atmospheric oxidation. Figure 2(b) is an XPS scan for the carbon peak; PA-treated Si exhibits strong peak at 285.5 eV (solid line) but no such peak is observed on bare Si (dashed line). This confirms chemical bonding of PA molecules to the Si surface. Thermal treatment of the Si(100) surface with PA molecules giving well ordered organic monolayer is reported by Saito *et al* [24]. The thickness of the PA monolayer by ellipsometric measurements was found to be 0.6 nm, which is close to the values reported for these molecules on silicon surfaces [36] (thickness was estimated by taking the refractive index $n = 1.42$ for organic molecules) [37]. According to semi-empirical calculations the thickness of PA, for a vertical orientation (i.e. for zero degree tilt), on silicon should be 0.67 nm [24]. Our measured values are slightly less, suggesting the possibility of slight tilt in molecules against the Si surface. The oxide thickness on bare silicon was measured to be 1.4 nm.

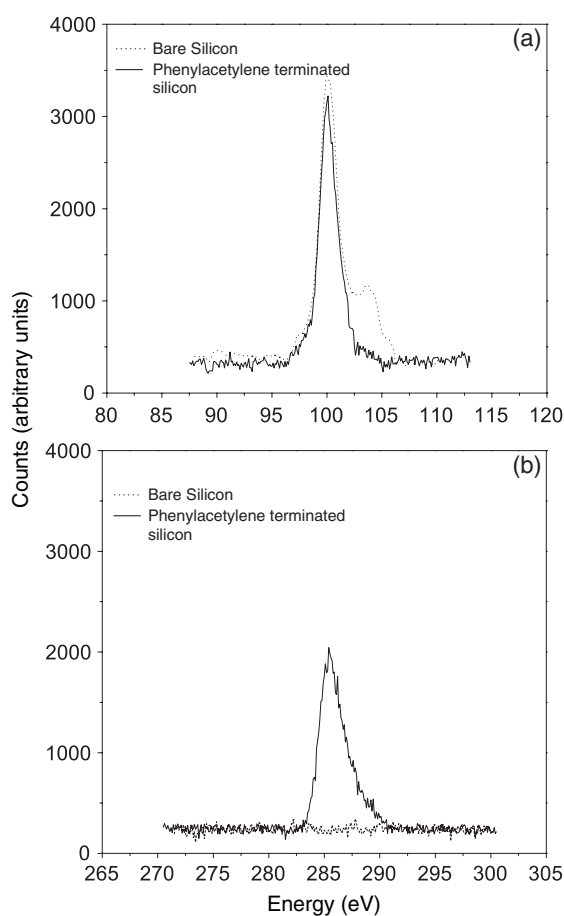


Figure 2. XPS spectra of (a) Si-2p peaks at 99.6 eV for Si:C₈H₆ (solid line), bare silicon (dashed line), (b) carbon peak at 285.5 eV for Si:C₈H₆ (solid line), with no peak for the bare silicon surface (dashed line).

3.2. Current–voltage measurements

To study the effect of electric current, pristine junctions were first subjected only to low current ($\pm 10 \mu\text{A}$) and then to high current (1 mA in forward region) measurements. Both dark and photoconductivity (under blue and white lights) were studied. Surface properties of silicon can be best explored by confining the photoexcitation close to the surface region; for this purpose we used a high intensity blue LED as the excitation source ($\lambda = 467 \text{ nm}$, characterized by an Ocean Optics spectrophotometer) which can generate charge carriers to a depth of about $0.3 \mu\text{m}$ in silicon [38], whereas white light (halogen lamp) excites charge carriers deep inside the semiconductor.

Figure 3(a) shows low current I – V curves in the dark for Si:H–Hg and Si:C₈H₆–Hg junctions. The curves of the two junctions exhibit a typical Schottky behavior with a rectification ratio of more than 10^2 . The current–voltage curve becomes narrower in molecular modified junctions than in Si:H–Hg junctions. The thermionic current in metal–molecule–semiconductor junctions, by considering the molecule as a thin tunneling barrier, is given

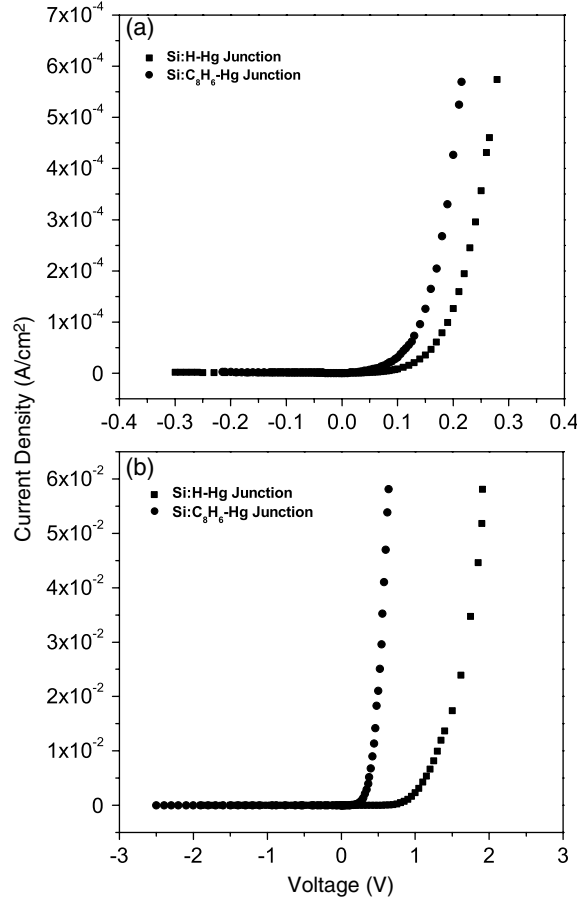


Figure 3. I - V curves in the dark for Si:H and Si:C₈H₆ surfaces: (a) low current, (b) high current.

by [39]

$$J = A^* T^2 \exp\left(-\frac{q\phi_{\text{eff}}}{kT}\right) \exp\left(\frac{qV}{nkT}\right) \left[1 - \exp\left(-\frac{qV}{kT}\right)\right] \quad (1)$$

where J (A cm⁻²) is the current density, A^* is the Richardson constant (32 A K⁻² cm⁻² for p-type Si), ϕ_{eff} (eV) is the effective barrier height, kT is the thermal energy, n is the ideality factor and is equal to 1 (if the charge transport is entirely by thermionic emission process), ϕ_{eff} is the effective barrier height for majority carriers to overcome the barrier in the presence of an interfacial layer and equals $\phi_b + (kT/q)\beta d$, where ' ϕ_b ' is the Schottky barrier between the metal and semiconductor, ' β ' and ' d ' are the structure dependent attenuation factor and thickness of the molecular layer. From the slope and intercept of $\ln[J/(1 - \exp(qV/kT))]$ versus V plots, the effective barrier height and ideality factor are estimated for the two junctions. With the help of Cheung's plots, the series resistance for different junctions was also estimated [40]. Calculated values of junction parameters for low current are given in table 1. The effect of chemical modification on the I - V behavior can be seen from the tabulated values. Departure of the ideality factor from 1 indicates that the transport mechanism is not entirely due to thermionic emission. The presence of PA molecules on the Si surface has reduced both the ideality factor and barrier height compared with the Si-H junction, indicating that the presence

Table 1. The various parameters of metal–molecule–semiconductor junctions estimated by I – V and C – V measurements.

Sample	Barrier height 'eV' (I – V)		Ideality factor ' n '		Series resistance ' R_s ' (Ω cm)	Barrier height 'eV' (C – V)	V_{d0} 'V'	Surface state density (10^{12} eV $^{-1}$ cm 2)
	Low current	High current	Low current	High current				
Si–H	0.824	0.91	1.62	2.8	66	0.60	0.32	0.205
Si–C $_8$ H $_6$	0.79	0.82	1.35	1.48	25	0.38	0.1	1.21

of conjugated molecules between metal and semiconductor enhances charge transport with low effective series resistance.

After low current, the junctions were subjected to high current measurements (up to 1 mA in the forward region). Figure 3(b) shows normal I – V plots for the two junctions in the dark. The plots exhibit Schottky behavior, Si:H–Hg junctions are non-ideal in the forward region, i.e. curves extend to a higher voltage; in contrast to this, Si:C $_8$ H $_6$ –Hg junctions are much sharper and are more ideal. Calculated values of the ideality factor and barrier height for high current measurements are given in table 1. In this regime the data deviate more from Cheung's plot, hence the series resistance was not estimated. The stability of molecular junctions was tested for 8 days and they were found to be quite stable in the low current limit. However, in the high current limit there was a small shift in voltage to the higher side (i.e. it drifted from 0.612 to 0.65 V at 1 mA).

Further photoconductivity measurements were carried out on these junctions with blue and white lights. Figure 4(a) is a logarithmic plot for Si:H–Hg junctions in dark, blue and white lights in the reverse region of device. Similar curves are shown in figure 4(b) for Si:C $_8$ H $_6$ –Hg junctions. The following are the notable features of these plots: (a) chemical modification reduces the leakage current, (b) under white light illumination both the junctions show equal response, (c) there is complete quenching of blue light photoconductivity in molecular junctions. It can be summarized that bonding of PA to the Si surface creates surface states whose energy position must be deep into the gap. They may act as slow traps and quench the surface photoconductivity. These are confined to the interface between the semiconductor and molecules as the other interface, i.e. that between Hg and molecules, is atomically plane and free from such states [41, 42]. Detailed studies like deep level transient spectroscopy of surface states are required to understand surface states. Quenching of blue light photoconductivity will be further discussed in the next section on capacitance–voltage measurements.

3.3. Capacitance–voltage measurements

Theoretically it has been well established that the capacitance measurements of heterostructures are extremely sensitive to interface states [43]. By measuring capacitance as a function of voltage and frequency, not only the bulk properties but also the interfacial properties of junctions can be well understood. Hence, immediately after low current measurements (before being subjected to high current I – V measurements), these junctions were subjected to C – V measurements for different frequencies (between 500 Hz and 1 MHz, for five different values). Figure 5(a) displays the results that are obtained on Si:H–Hg junctions in the dark; for clarity only the two curves one at 500 Hz and another at 1 MHz are shown. These junctions show great disparity between the two curves in the forward region, being least around zero bias and going to zero below -0.17 V in the reverse bias. Similar curves for Si:C $_8$ H $_6$ –Hg junctions are shown in figure 5(b). Here also, the difference between the two curves builds

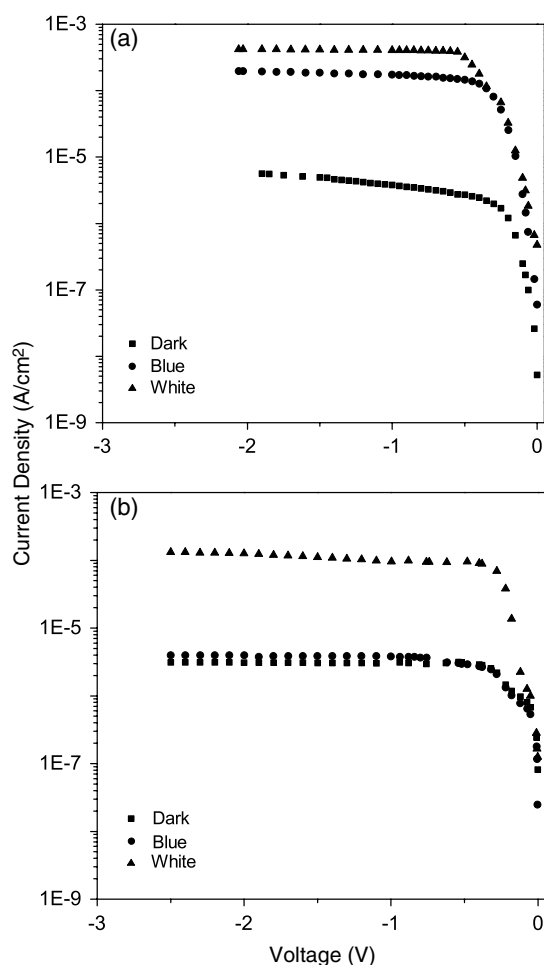


Figure 4. Comparison of current–voltage curves under reverse bias under dark, white and blue lights for (a) Si:H–Hg and (b) Si:C₈H₆–Hg junctions.

up with forward voltage, but the change is much smaller than for Si:H–Hg junctions. It is important to note that the point of convergence is quite different in the two cases, around -0.17 V in Si:H–Hg and -0.3 V in Si:C₈H₆–Hg junctions. Similar measurements have also been reported on Hg–Si junctions with SiO₂, C₁₂ and C₁₂–SiO₂ as an interfacial layer between metal and semiconductor [42]. These studies reveal that the fixed interfacial charges induces a gap between two frequency curves in the region of reverse bias. In the present case, Si:H–Hg junctions exhibit a narrower gap between the two curves than Si:C₈H₆–Hg junctions and finally merge well inside the reverse region. This indicates that there is a permanent electric charge at the interface between Si and organic molecules. A permanent electric charge has been clearly observed in Kelvin probe force microscopy measurements on thermally deposited PA molecules on Si [24]. The bonded molecules possess a permanent dipole-moment and these monolayers enhance electrical conductivity between the metal and semiconductor. Hence, it is expected in the present measurements that the bonding of PA molecules to the Si surface leads to an extra density of surface states.

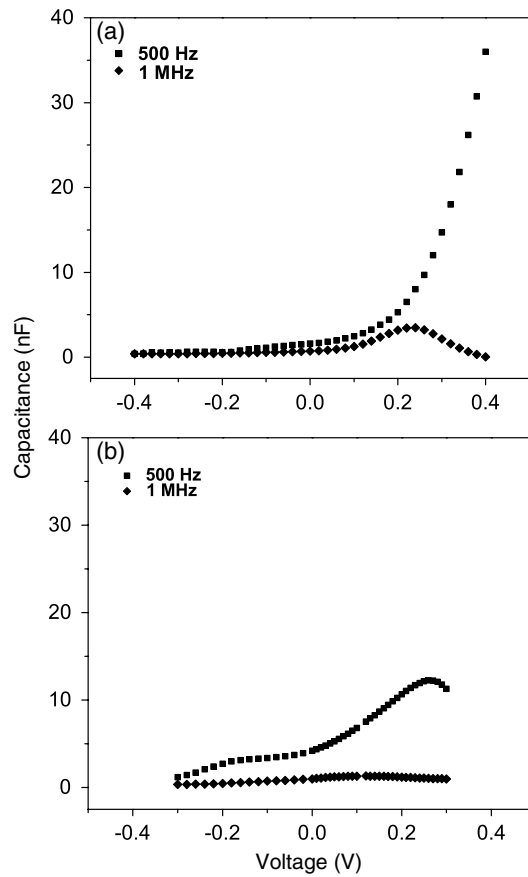


Figure 5. Capacitance–voltage curves in the dark for (a) Si:H–Hg junctions and (b) Si:C₈H₆–Hg junctions.

The typical relation between capacitance and voltage of the Schottky diode can be used to estimate the parameters of metal–molecule–semiconductor junctions, which is given by [39, 43]

$$\frac{1}{C^2} = \frac{2(V_{d0} - V)}{qA^2\epsilon_s\epsilon_0N} \quad (2)$$

where V_{d0} is surface potential, V the applied voltage, q the electron charge, A the area of contact between metal and the silicon surface, ϵ_0 the permittivity of free space, ϵ_s the dielectric constant of the semiconductor and N the acceptor concentration of the semiconductor. The slope and intercept of the Mott–Schottky plots ($1/C^2$ versus V) under reverse bias are used to estimate the surface potential, the barrier height of different junctions and the bulk doping density of Si. The estimated values of doping density, within an experimental error, are close to the supplier's data ($2\text{--}3 \times 10^{15} \text{ cm}^{-3}$) in the present case. The table indicates that both barrier height and surface potential are significantly reduced (more than 60%) upon the chemical modification of Si.

Interface states, in general, are slow and respond differently at lower and higher frequencies of applied ac signal. They follow the signal at lower frequency and the total capacitance of a junction is the sum of interface and space charge capacitances. But at

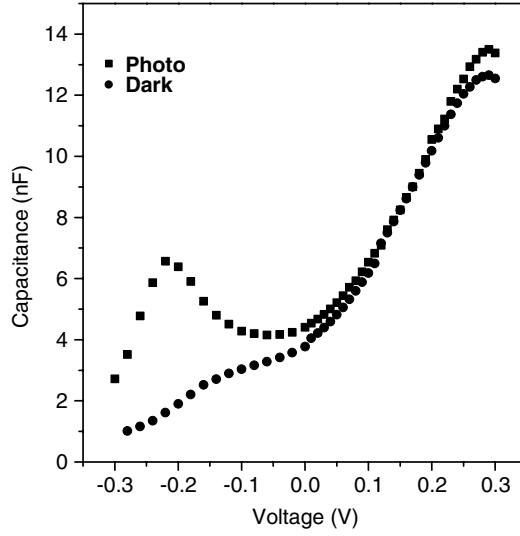


Figure 6. Comparison of the capacitance curve at 500 Hz for Si:C₈H₆-Hg junctions in dark (solid circles) and white light illumination (solid squares).

higher frequencies the contribution to capacitance comes only from the space-charge region. Therefore, the difference in the magnitude of capacitance at low and high frequencies is a direct measure of the interface state density. Under this consideration, the interface density of states is given by [44]

$$D_{it} = \sqrt{\frac{q\epsilon_s\epsilon_0 N}{2V_d}} \left[\frac{(C_{LF} - C_{HF})}{qC_{LF}} \right] \quad (3)$$

where C_{LF} and C_{HF} are the capacitance at lower and higher frequencies at the applied bias V , V_d is the voltage dependent surface potential and other terms have their usual meaning. Further, the relation between surface potential and applied voltage is $V_d = V_{d0} - (V/n)$, where n is the ideality factor of the junction. Calculated values of interface density and surface potential, at zero voltage, for the two junctions are shown in table 1. The two frequency curves were used to calculate D_{it} as a function of energy difference between the surface Fermi energy (E_F^S) and the top of valence band, since the E_F^S can move in the gap under applied voltage. These values of D_{it} are quite close to the reported values in the literature on metal-molecule-semiconductor junctions [45]. It is noted that surface states increase significantly as E_F^S moves closer to the valence band and they decrease rapidly as it resides deeper into the gap. These calculations also show that the mid-gap surface states are high in Si-C₈H₆ interface. Therefore, it can be concluded that the chemical bonding of PA to Si surfaces creates a uniform surface charge whose energy positions are deeper inside the gap; these act as recombination centers for photogenerated carriers.

The set-up was also used to measure the photocapacitance of these junctions under constant white light illumination. Low frequency dark and photocapacitance curves at 500 Hz for Si:C₈H₆-Hg junctions are shown in figure 6. The curve on the Si:H-Hg junction is quite similar to its dark counterpart, except for a small and uniform increase in the capacitance values (hence it is not shown in the figure). It is clear from these curves the photocapacitance exhibits well-defined peaks in the reverse region. The position and intensity of this peak is highly frequency dependent and goes to zero at high frequency (1 MHz). Photocapacitance of

TiO₂, WS₂ and MoS₂ electrodes in an electrochemical cell has been reported [46, 47]. These measurements show only a uniform rise in the capacitance under illumination and this extra capacitance has been accounted for in charging of surface traps. A report on InP point contact Schottky diodes [48] shows that these junctions exhibit well-defined peaks in photocapacitance and are attributed to surface defects positioned at discrete energy levels in the gap. Therefore, the photocapacitance peaks in our measurements are due to additional surface states that are created by the presence PA molecules on the Si surface. They respond only at low frequency and hence are slow traps for photocarriers. Under photoexcitation they capture the charge carriers and contribute an extra capacitance and are also responsible for the quenching of photoconductivity.

4. Summary

Passivation of the Si(100) surface by PA molecules is carried out to study the effect of organic molecules on electronic devices. Thermally bonded PA molecules were used to construct metal–molecule–Si junctions via soft electrical contact. These studies show that thermally treated junctions are more ideal and more conducting than Si:H–Hg junctions; this can be attributed to vertical alignment of PA molecules on the Si surface. Further, in these investigations it is observed that the molecule–Si interface features surface states that are charged and are created deep inside the energy gap; these are responsible for the observed quenching of photoconductivity in these junctions.

Acknowledgments

We acknowledge the Department of Science and Technology, Government of India, for funding this project (under the contact no. SR/S2/CMP/-28/2002). One of the authors, R K Hiremath, is grateful for the fellowship given under the Physics Department's UGC-DSA Programme (Phase–III). We also wish to thank Professor G U Kulkarni, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, for XPS measurements and Ms C Shweta, Department of Physics, National Instruments Facilities, IISc, Bangalore, for ellipsometric measurements.

References

- [1] Linford M R, Fenter P, Eisenberger P M and Chidsey C E D 1995 *J. Am. Chem. Soc.* **117** 3145
Sieval A B, Linke R and Sudholter Z H 2000 *Adv. Mater.* **12** 1457
Boukherroub R and Wayner D D M 1999 *J. Am. Chem. Soc.* **121** 11513
- [2] Hamers R J 2001 *Nature* **412** 489
- [3] Cohen R, Kronik L, Vilan A, Shanzer A and Cahen D 2000 *Adv. Mater.* **12** 33
- [4] Kruger J, Bach U and Gratzel M 2000 *Adv. Mater.* **12** 447
- [5] Lisensky G C, Penn R L, Murphy C J and Ellis A B 1990 *Science* **248** 840
Lauerhaas J M and Sailor M J 1993 *Science* **261** 1567
- [6] Sweryda-Krawice B, Chandler-Henderson R R, Coffey J L, Rho Y G and Pinnizzotto R F 1996 *J. Phys. Chem.* **100** 13776
- [7] Many A, Goldstein Y and Grover N B 1965 *Semiconductor Surfaces* (Amsterdam: North-Holland)
- [8] Luth H 1998 *Surfaces and Interfaces of Solid Materials* (Berlin: Springer)
- [9] Buriak J M 2002 *Chem. Rev.* **102** 1271
- [10] Herdt G C and Czanderna A W 1994 *J. Vac. Sci. Technol. A.* **12** 2410
- [11] Brook M A 2000 *Silicon in Organic, Organometallic and Polymer Chemistry* (New York: Wiley)
Patai S and Rappaport Z (ed) 1989 *The Chemistry of Organic Silicon Compounds* (New York: Wiley)
- [12] Terry J, Linford M R, Wigren C, Cao R, Pianetta P and Chidsey C E D 1999 *J. Appl. Phys.* **85** 213

- [13] Sung M M, Klulh G H, Yauw O W and Maboudian R 1997 *Langmuir* **13** 6164
- [14] Linford M R and Chidsey C E D 1993 *J. Am. Chem. Soc.* **115** 12631
- [15] de Villeneuve C H, Pinson J, Bernard M C and Allongue P 1997 *J. Phys. Chem. B* **101** 2415
- [16] Yu H J, Morin S and Wayner D D M 2000 *J. Phys. Chem. B* **104** 11157
- [17] Shaw J M and Seidler P F 2001 *IBM J. Res. Dev.* **45** 3
- [18] Hacker C A and Hamers R J 2003 *J. Phys. Chem. B* **107** 7689
Hung L S and Chen C H 2002 *Mater. Sci. Eng. R* **39** 143
- [19] Tao F, Wang Z H, Lai Y H and Xu G O 2003 *J. Am. Chem. Soc.* **125** 6687
- [20] Kim K Y, Song B K, Jeong S and Kang H 2003 *J. Phys. Chem. B* **107** 11987
- [21] Pluchery O, Coustel R, Witkowski N and Borensztein Y 2006 *J. Phys. Chem. B* **110** 22635
- [22] Seival A B, Opitz R, Maas H P A, Schoeman M G, Meijer G, Vergeldt F J, Zuilhof H and Sudholter E J R 2000 *Langmuir* **16** 10359
- [23] Zhang J F, Cui C Q, Lim T B, Kang E T and Neoh K G 1999 *Chem. Mater.* **11** 1061
- [24] Saito N, Hayashi K, Sugimura H and Takai O 2003 *Langmuir* **19** 10632
- [25] Hsu J W 2005 *Mater. Today* **42** (July/August) (review article)
- [26] Xue Y Q, Datta S and Ratner M A 2001 *J. Chem. Phys.* **115** 4292
- [27] Fauple F, Willecke R and Thran A 1998 *Mater. Sci. Eng. R* **22** 1
- [28] Birgerson J, Fahlman M, Broms P and Salaneek W R 1996 *Synth. Met.* **80** 125
- [29] Reed M A, Zhou C, Muller C J, Burgin T P and Tour J 1997 *Science* **278** 252
Park J, Pasupathy A N, Goldsmith J I, Chang C, Yaish Y, Petta J R, Rinkoski M, Sethna J P, Abruna H D, McEuen P L and Ralph D C 2002 *Nature* **417** 722
Reichert J, Oehs R, Beckmann D, Weber H B, Mayor M and Lohneysen H v 2002 *Phys. Rev. Lett.* **88** 176804
- [30] Vilan A and Cahen D 2002 *Adv. Funct. Mater.* **12** 795
- [31] Andres R P, Bein J, Dorogi M, Feng S, Henderson J I, Kubiak C P, Mahoney W, Osifchin R G and Reifenberger R 1996 *Science* **272** 1323
Cui X D, Primak A, Zarate X, Jomfohr J, Sankey O F, Moore A L, Moore J A, Gust D, Harris G and Lindsay S M 2001 *Science* **294** 571
- [32] Holmlin R E, Haag R, Chabinye M L, Ismagilov R F, Cohen A E, Jerfort A, Rampi M A and Whitesides G M 2001 *J. Am. Chem. Soc.* **123** 5075
- [33] Loo Y-L, Willet R L, Baldwin K W and Rogers J A 2002 *J. Am. Chem. Soc.* **124** 7654
- [34] Shin J, Geib K M and Wilmsen C W 1991 *J. Vac. Sci. Technol B* **9** 2337
- [35] Wittmer M and Freeouf J L 1992 *Phys. Rev. Lett.* **69** 2701
- [36] Li Z and Lieberman M 2001 *Langmuir* **17** 4887
- [37] Lheveder C and Meunier J 2000 *Physical Chemistry of Biological Interfaces* ed B Adam and N Willem (New York: Dekker) pp 559–75
- [38] Sze S M 2005 *Physics of Semiconductor Devices* 2nd edn (New York: Wiley) p 750
- [39] Selzer Y, Solomon A and Cahen D 2002 *J. Phys. Chem. B* **106** 10432
- [40] Cheung S K and Cheung N W 1986 *Appl. Phys. Lett.* **4a** 85
- [41] Faber E J, de Smet L C P M, Olthuis W, Zuilhof H, Sudholter E J R, Bergveld P and van den Berg A 2005 *ChemPhysChem* **6** 2153
- [42] Liu Y J and Yu H Z 2003 *J. Phys. Chem. B* **107** 7803
- [43] Rhoderick E H and Williams R H 1988 *Metal-Semiconductor Contacts* 2nd edn (Oxford: Clarendon)
- [44] Chattopadhyay P and Ray Chaudhuri B 1993 *Solid State Electron.* **36** 605
Chattopadhyay P 1996 *Solid State Electron.* **39** 1491
- [45] Kim N Y and Laibinis P E 1999 *J. Am. Chem. Soc.* **121** 7162
- [46] Hagfeldt A, Bjorksten U and Gratzel M 1996 *J. Phys. Chem.* **100** (20)
- [47] Memming R, Keily J J and Connolly (ed) 1980 *Photochemical Conversion and Storage of Solar Energy* (New York: Academic) p 243
Kelly J J and Memming R 1982 *J. Electrochem. Soc.* **129** 730
- [48] Oyama Y, Nishizawa J, Kimura T and Tanno T 2006 *Phys. Rev. B* **74** 235210