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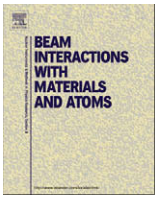

Ion-scattering analysis of self-assembled monolayers of silanes on organic semiconductors

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ABSTRACT

We describe new Rutherford Backscattering Spectroscopy (RBS) measurements to explore the surface chemistry associated with the growth of self-assembled monolayer (SAM) molecules on conducting organic films. The report includes a description of the optimization of both substrates and RBS scattering parameters to appropriately analyze these novel and damage susceptible structures. Our RBS measurements reveal that the final surface stoichiometry is consistent with a specific model of hydrolyzed and crosslinked trichlorosilanes that form a dense two-dimensional network (a monolayer) at the surface of small-molecule organic semiconductors and a bulk SAM network in the case of conjugated polymer films. Organic semiconductors used in this study are thin films of *rubrene* (a small molecule semiconductor ($C_{42}H_{28}$)) and *poly(3-hexyl)thiophene* (P3HT) (a conjugated polymer $(C_{10}H_{18}S)_n$). As a substrate we used a thick (1 μm) film of *parylene* (a non-conjugated polymer $(C_8H_8)_n$) deposited on Si (1 0 0) wafers. The SAM molecules used to functionalize the organic semiconductor films are fluoroalkyl trichlorosilane (FTS) ($C_8(H_4F_{13})SiCl_3$) and octyltrichlorosilane (OTS) ($C_8H_{17}SiCl_3$). Quantitative detection of medium and small-mass elements, such as O, F, Si, S and residual Cl is demonstrated and used to elucidate the surface chemistry in these novel organic systems.

1. Introduction

Rutherford Backscattering Spectroscopy (RBS) is one of the surface analytical techniques that can be efficiently used for elemental analysis of materials surfaces [1]. While RBS has played a significant role in the development of inorganic semiconductor structures, its application to organic films has been more problematic. The active development of the new organic semiconductor materials creates a demand for analytical methods capable to measure a composition of the organic thin films with high accuracy and high depth resolution. Both of these requirements are potential attributes of RBS.

In this work we apply RBS analysis to some of the most intriguing organic materials systems. Rubrene ($C_{42}H_{28}$) is a small-molecule organic semiconductor of great current interest due to the high field-effect mobility [2,3]. Among conjugated polymers, P3HT is the most commonly used archetypal material popular for its processability and good carrier mobility [4,5]. The electrical conductivity of these materials can be increased by orders of magnitude when the surface is *hole* doped using a self-assembled monolayer (SAM) of FTS ($C_8(H_4F_{13})SiCl_3$) [6,7]. The model of SAM molecules attachment to the surface of these organic materials is still unknown and a subject of fervent research. Our RBS investigation can, thus, provide direct evidence for the complex chemical processes associated with the formation of these SAM/organic couples.

Usually, RBS faces several limitations when used on organic thin films. The ion beam may cause film damage, change its composition and produce desorption of the surface species. Furthermore, this technique is limited by low RBS cross-section for the low mass elements usually found in the organic materials while a substantial background from typical sample substrates may limit accuracy.

In this work we demonstrate the detection of small amounts of the low mass elements (monolayers of O, F, Si) in the self-assembled monolayers grown on several different organic thin films. We use RBS in normal and glancing angle detection mode in combination with a selected special substrate structure. Depending on the organic film thickness and the structure of the SAM, we configure a proper RBS geometry with glancing exit angle detection to optimize the surface sensitivity and depth resolution (Fig. 1b). Furthermore, to suppress the RBS background from the substrate (in our case Si), we added a layer of parylene, the organic non-conjugated polymer, between the substrate and the SAM functionalized organic thin film of interest (Fig. 1c). This geometry formed a

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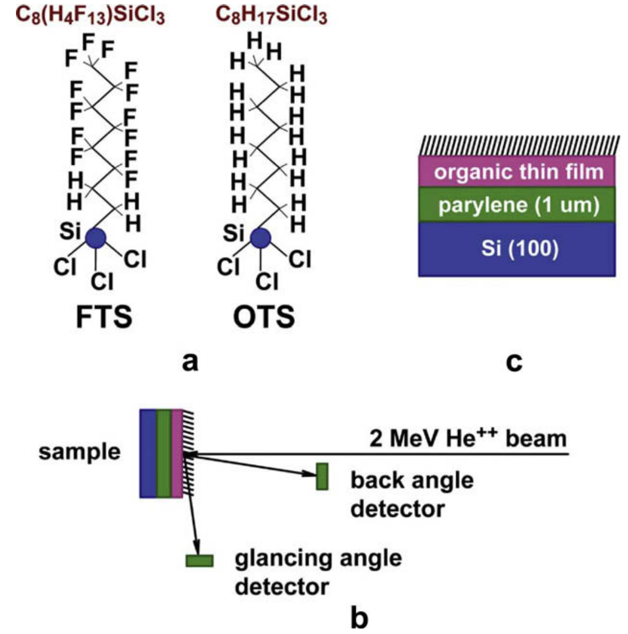

Fig. 1. (a) Chemical structure of FTS, (tridecafluoro-1,1,2,2,-tetrahydorooctyl) trichlorosilane ($C_8H_4F_{13}SiCl_3$) and OTS, octyltrichlorosilane ($C_8H_{17}SiCl_3$) self-assembled monolayer (SAM) molecules used to functionalize organic thin films. (b) RBS experimental setup showing the position of the back and glancing angle detectors. (c) General sample structure used in this study.

substantial total thickness of up to 1.5 μm of organic films on Si substrates.

In this type of structure, the energy of the RBS signal coming from the Si substrate is reduced substantially, so that RBS signals of O, F, Si, S or Cl, from the organic thin film and the SAM can be easily detected. Additionally, glancing angle detection is used in order to increase the depth resolution and sensitivity of the measurements.

2. Experimental

Semiconductor quality Si (1 0 0) wafers cut into 1 × 1 cm^2 pieces were used as a substrate for all the samples. The silicon substrate was coated with a non-conjugated polymer parylene ($(C_8H_8)_n$) (approx. 1 μm thick) via vapor deposition process in a vacuum of around 10^{-3} Torr. The details of the parylene deposition process are described in Ref. [8]. Thin films (thickness of around 20–30 nm) of rubrene ($C_{42}H_{28}$) or poly(3-hexyl)thiophene, P3HT, ($(C_{10}H_{18}S)_n$) were spin coated from solution onto the surface of parylene. The rubrene solution (0.5 wt%) was prepared by dissolving Sigma–Aldrich sublime grade rubrene powder in toluene. The P3HT solution (0.5 wt%) was prepared by dissolving Alfa Aesar P3HT powder in chloroform. Both powders were used as received without further purification.

Self-assembled monolayer molecules used in this study to functionalize the organic thin films are (tridecafluoro-1,1,2,2,-tetrahydorooctyl)trichlorosilane – $C_8H_4F_{13}SiCl_3$ (designated as FTS) and octyltrichlorosilane – $C_8H_{17}SiCl_3$ (OTS). Chemical structures of these molecules are shown in Fig. 1a. Deposition of the SAMs on parylene, rubrene and P3HT thin films was done from a vapor phase in a separate chamber under a vacuum of 10^{-3} Torr until a full surface coverage was attained. The SAM deposition process is described in detail in Ref. [6]. The RBS analysis is performed in a standard RBS chamber under a vacuum of about 10^{-6} Torr using two commercial Si surface barrier detectors: one at about 155° and other at about 100° scattering angle (shown in Fig. 1b). A 2 MeV He^{++} ion beam from 1.7 MV tandem accelerator is used with an ion current of about 2–3 nA and a relatively large ion beam spot of about 3 mm × 3.4 mm in order to reduce the ion beam damage of the organic films. Composition spectra have been recorded after different ion fluences (10^{-6} C, 2 × 10^{-6} C, 4 × 10^{-6} C, 8 × 10^{-6} C and 16 × 10^{-6} C) to monitor possible ion beam induced modification of the sample. Spectra simulation was done using the SIMNRA program.

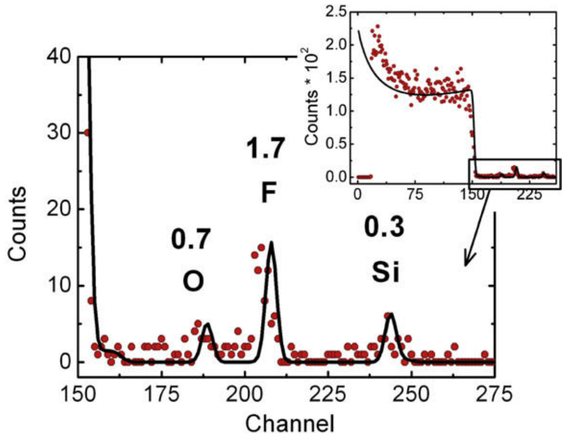

Fig. 2. 2 MeV He RBS spectrum collected with the detector in the glancing angle position from a Si/parylene sample functionalized with FTS SAM. The thickness of the parylene layer is 1 μm. The numbers shown above the peaks indicate measured surface coverage in 10^{15} atoms/cm^2. The He ion fluence is 2 μC.

3. Results and discussion

The RBS spectrum collected in the glancing angle geometry from Si covered with 1 μm of parylene and functionalized with FTS ($C_8(H_4F_{13})SiCl_3$) is shown in Fig. 2. Note that O, F and Si peaks are in the background-free region due to the glancing angle geometry and presence of the thick (1 μm) parylene layer. Quality of the RBS fit is limited by low counts in F, O and Si peaks and a residual background counts, but it allows estimating atomic ratios and elements involved. Positions of O and F peaks can be shifted due to surface contaminations as the RBS depth sensitivity is high in this glancing angle geometry. The F/Si atomic ratio measured is about 6, which is two times lower than 13 expected from FTS chemical formula. We address this issue of low F/Si ratio later in the paper. There is no chlorine detected, which is in agreement with our tentative attachment model for trichlorosilane molecules where Cl is lost during the hydrolysis reaction and removed in the form of HCl vapor (as shown in Fig. 3a). Such hydrolysis is known to occur with trichlorosilanes in contact with a residual water vapor in vacuum chambers or water molecules physisorbed at the surface of the samples [9]. The presence of the oxygen peak supports the attachment model; however the O/Si ratio is 2.3, i.e. slightly greater than the expected 2 for an ideal structure shown in Fig. 3b. The width and the position of F and Si peaks indicate that FTS molecules do not penetrate into the parylene film, but rather remain at its surface.

Similar RBS results are obtained in the back angle geometry from Si substrates covered with a 1 μm thick parylene layer and rubrene thin film functionalized with FTS (Fig. 4). This spectrum was collected for a 2 MeV He ion beam fluence of 8 × 10^{-6} C; the F peak corresponds to 17.8 × 10^{15} F atoms/cm^2, O peak corresponds to 6.2 × 10^{15} atoms/cm^2 and the Si peak corresponds to 2.2 × 10^{15} Si atoms/cm^2. This result indicates that the measured O/Si atomic ratio is 2.8, i.e. greater than the expected value of 2.0. This might be due to the presence of rubrene oxide formed

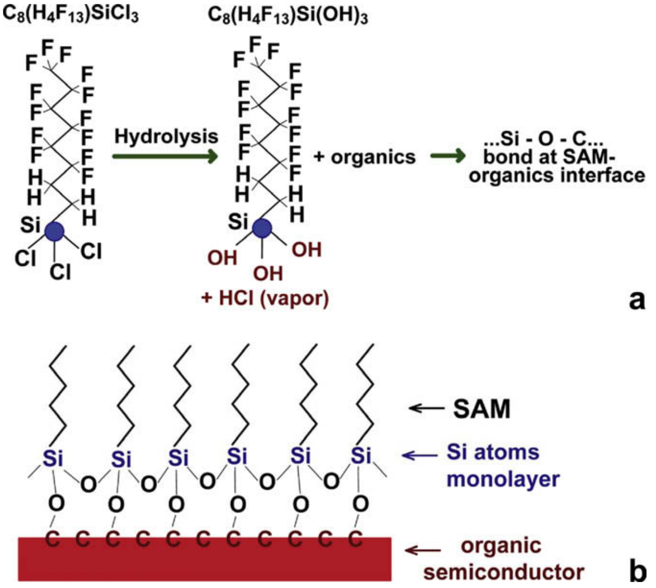

Fig. 3. (a) Our tentative surface chemistry model of the trichlorosilane molecule attachment to the surface of the organic material. (b) Interface between the organic material and the trichlorosilane self-assembled monolayer (SAM) in our tentative attachment model.

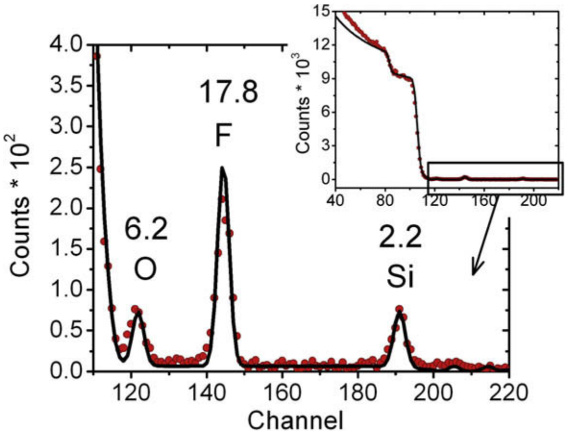

Fig. 4. 2 MeV He RBS spectrum collected with the detector in the back angle position from a Si/parylene/rubrene thin film sample functionalized with FTS SAM. The thickness of parylene and rubrene thin films is 1 μm and 20 nm, respectively. The numbers shown above the peaks indicate the measured surface coverage in 10^{15} atoms/cm^2. This spectrum was collected until 2 MeV He ion beam fluence reach 8 μC (80 μC/cm^2).

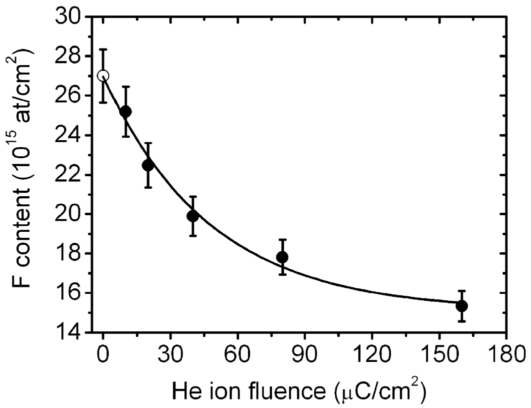

Fig. 5. Fluorine surface coverage measured on Si/parylene/rubrene sample functionalized with FTS SAM as a function of RBS He ion fluence. Open circle point shown in the figure is extrapolated using the exponential decay fit (solid black line) of measured full circle points to obtain initial fluorine peak intensity.

in the spin coated rubrene films prior the FTS treatment or oxygen containing contaminants on the surface. The F/Si atomic ratio is 8.1, which is smaller than expected 13 from the molecular formula. Note that, as in the case of parylene, there is no Cl detected but there is a small amount of S (about 0.15 × 10^{15} S atoms/cm^2). Again, as in the case of parylene, FTS molecules remain at the surface of the rubrene thin film and there is no detectable penetration of FTS into the film. This conclusion is supported by width and position of F, Si and O peaks in glancing angle detector spectrum (not shown).

In order to study possible changes in the concentration of the detected elements (O, F, Si) as a function of He ion fluence, the rubrene sample was measured in several fluence steps. After each fluence step the RBS spectrum is recorded and added to the spectrum taken in the previous step. The results of these multiple measurements show that the O and Si peaks intensities are proportional to He ion fluence (not shown) and the RBS measured concentrations are not dependent on the He ion fluence for the low current densities used in this work.

In contrast to O and Si, the F peak intensity is not proportional to the He ion fluence. The fluorine concentration after each measurement is calculated and the results are shown in Fig. 5. It is clear that some F is lost during the measurement, and the loss is greater at higher fluences. The fluorine concentration, extrapolated to the zero He ion fluence, is 27 × 10^{15} F atoms/cm^2 (open circle point in Fig. 5) by fitting the measured data (full circle points in Fig. 5) with the exponential decay function. The F/Si atomic ratio obtained from this extrapolation is 12.3 ± 0.8 and agrees well with the expected ratio for the FTS molecules, which is 13. These results indicate that F is released from FTS during the RBS measurement due to the ion beam induced desorption and special experimental arrangements must be used (large beam spot area, in our case 0.1 cm^2 and a substantial detector solid angle, in our case 0.02 steradians) in order to reduce ion beam effects. For accurate results multiple measurements are recommended and extrapolation to zero He ion fluence is suggested in order to properly estimate the initial F concentration.

The absolute values of F, O and Si concentrations indicate that in the case of solution deposited rubrene the amount of FTS noticeably exceeds the surface density of rubrene molecules in a well ordered rubrene crystal, 10^{14} cm^{-2}. For an ideal single crystal coated with an FTS monolayer, one would expect the density of SAM approaching this value. The higher concentration of FTS observed in this case is likely related to a polycrystalline or even amorphous nature of this semiconductor film prepared from solution. Such samples have been used in this study for the sake of increasing the sample's area. High surface roughness results in a much greater effective concentration of the SAM, indicating the desirability of measurement on flat and possibly single crystal, material.

An RBS back angle geometry spectrum from Si covered with 1 μm of parylene and thin film of conjugated polymer P3HT $(C_{10}H_{18}S)_n$ functionalized with FTS molecules is shown in Fig. 6. The F/Si atomic ratio is about 12, close to the expected FTS composition. There is a small Cl peak indicating that in this case not all Cl have been removed from the sample and there is 8% of initial Cl still present in the film. This can be the result of an incomplete hydrolysis of FTS or a residual HCl trapped in the film. The observed S peak is from the thiophene ring of P3HT polymer, and it is used to gauge the amount of P3HT monomers present in the sample. From the glancing angle RBS spectrum of the same sample (Fig. 7) the position and the width of F, Si and S peaks indicate that

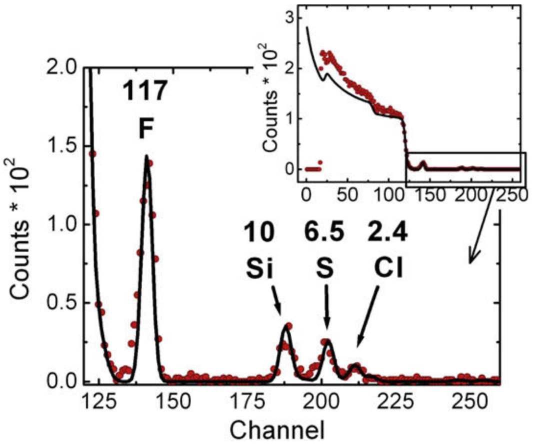

Fig. 6. 2 MeV He RBS spectrum collected with the detector in the back angle position from a Si/parylene/P3HT thin film sample functionalized with FTS SAM. The thickness of parylene film is 1 μm. The thickness of P3HT thin film before FTS growth is 20 nm. The numbers shown above the peaks indicate measured surface coverage in 10^{15} atoms/cm^2. The He ion fluence is 1 μC.

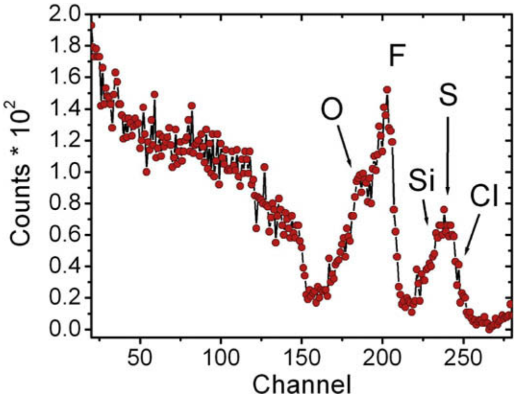

Fig. 7. 2 MeV He RBS spectrum collected with the detector in glancing angle position from a Si/parylene/P3HT thin film sample functionalized with FTS SAM molecules. The thickness of parylene film is 1 μm. The thickness of P3HT thin film before FTS growth is 20 nm. The He ion fluence is 2 μC. Please note broad and overlapping F, O, Si and S peaks indicating a bulk type of doping of the P3HT film with FTS.

FTS and P3HT are in the "alloy" form, i.e., P3HT film is bulk doped with FTS. This result is in a clear contrast with the previous cases of surface doping of parylene or rubrene. Such bulk doping is consistent with the optical "bleaching" effect observed in P3HT, in which FTS doped films become highly conducting with interband optical absorption of the polymer strongly suppressed making the samples almost completely transparent in the visible range [7]. Such behavior of FTS doping of P3HT is due to the highly porous morphology of conjugated polymers that consist of individual π-stacked nanofibrils and nanodomains [4,5].

To confirm that the RBS fluorine signal detected in these samples is coming from the FTS SAM layer itself, we also functionalized the same organic thin films (parylene, rubrene and P3HT) with non-fluorinated trichlorosilane (OTS) instead of fluorinated trichlorosilane (FTS) molecules. RBS spectra for OTS functionalized thin films (not shown) show no fluorine peak, confirming that the pronounced fluorine peak does originate from the FTS SAM.

4. Conclusions

Rutherford Backscattering Spectroscopy (RBS) measurements were conducted on several different types of organic materials functionalized with self-assembled monolayers of fluorinated trichlorosilane (FTS) and non-flourinated trichlorosilane (OTS) molecules. Organic materials included in this study were parylene – a non-conjugated polymer thin film, rubrene – a small molecule semiconductor thin film, and P3HT – a conjugated polymer thin film.

We conclude that RBS can be used as a tool for detection and quantitative elemental analysis in these organic systems with several experimental adjustments. To insure the stability of the organic material during the RBS measurement film proper experimental arrangements should be used (low He ion current, reasonably big ion beam spot and a substantial solid angle of the detector). Furthermore, use of the glancing angle detector improves the depth resolution of the measurement for very thin films and helps to reduce the RBS background coming from the substrate. This background was further reduced by adding a substantial (1 μm thick) parylene layer between the substrate and the functionalized organic thin film of interest.

Furthermore, from our RBS measurements we conclude that in the case of parylene and rubrene chemically modified thin films, FTS SAM molecules remain on the surface of the film, whereas for P3HT thin film there is significant penetration of the molecules into the film bulk.

The absence of Cl and presence of oxygen peak in RBS spectra, as well as the elemental ratios obtained from quantitative RBS analysis are in agreement with our tentative model of SAM attachment.

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