Diels–Alder chemistry at furan ring functionalized solid surfaces†

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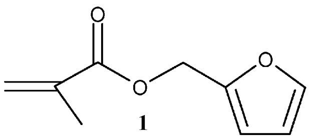
A substrate-independent method for Diels–Alder chemistry at solid surfaces is described for the first time.

Diels–Alder chemistry has previously been shown to occur at semiconductor surfaces in relation to potential application in microelectronics.[1] For instance, the Si(100) and Si(001) surfaces can undergo [4 + 2] cycloaddition reactions with 1,3-butadiene[2,3] and 1,3-cyclohexadiene[4] respectively. Diamond(100) surfaces have also been found to exhibit dienophile behaviour.[5,6] Other examples of surface Diels–Alder reactions include self assembled monolayers (SAMs)[7] and the immobilization of dyes.[8] A major drawback of earlier studies has been their limitation to substrate-specific chemistries which require several reaction steps.

Pulsed plasma polymerization is recognized as being a practical, substrate-independent route for functionalizing solid surfaces with specific chemical groups. Other advantages include the fact that this approach is quick (single step), solventless, energy efficient, and can be applied to a whole host of complex geometries (*e.g.* microspheres, fibres, tubes, *etc.*). In contrast to conventional continuous wave plasma polymerisation which is well known to give rise to the incorporation of a variety of functional groups at a surface (due to severe fragmentation of the precursor molecule within the electrical discharge[9]), pulsing the electric discharge on the ms–μs time scale has been shown to yield high levels of functional retention.[10,11] In mechanistic terms, this marked enhancement in selectivity can be ascribed to low levels of precursor fragmentation occurring during the short duty cycle on-period combined with conventional polymerization reaction pathways predominating within the much longer pulsed plasma off-period. Examples of well-defined molecularly tailored substrates produced by this method include perfluoroalkyl,[12] epoxide,[13] anhydride,[14] carboxylic acid,[15] cyano,[16] hydroxyl,[17] and amine[18] functionalised surfaces. The inherent excellent adhesion to the substrate of the chemical groups stems from surface activation during electrical discharge exposure. For the purposes of this investigation, furfuryl methacrylate (Structure **1**) has been chosen as the precursor for pulsed plasma polymerisation in order to provide furan ring functionalized surfaces, which are capable of participating in [4 + 2] cycloaddition reactions with simple alkenes (dienophiles) to form six membered rings.[19–21] This approach is an extension of earlier studies relating to tailoring solid surfaces with aromatic rings.[22–24]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A depletion of oxygen was noted by XPS at the surface of furfuryl methacrylate plasma polymer films deposited under continuous wave conditions onto glass slides; whereas pulsed plasma polymerization yielded a close match to the expected theoretical value, Table 1. Also the C(1s) envelope for the latter could be fitted to three different types of carbon environment, in accordance with the monomer structure: 285.0 eV ($-C_xH_y-$), 286.4 eV (–C–O), and 288.9 ((C=O)O) (in the ratio of 5.4 : 3.4 : 1.0 compared to the theoretical values of 5 : 3 : 1), Fig. 1. A π–π* shake-up satellite indicative of conjugation provided further evidence for structural retention of the furan ring during pulsed plasma deposition. In the case of continuous wave plasma polymerization, the oxidised carbon region in the C(1s) envelope

Table 1 XPS elemental percentage analysis of furfuryl methacrylate plasma polymers

Plasma polymer	% C	% O
Monomer (theoretical)	75	25
Continuous wave	80 ± 1	20 ± 1
Pulsed	75 ± 2	25 ± 2
Pulsed reacted with maleic anhydride (theoretical)	68.4	31.6
Pulsed reacted with maleic anhydride	70 ± 2	30 ± 2

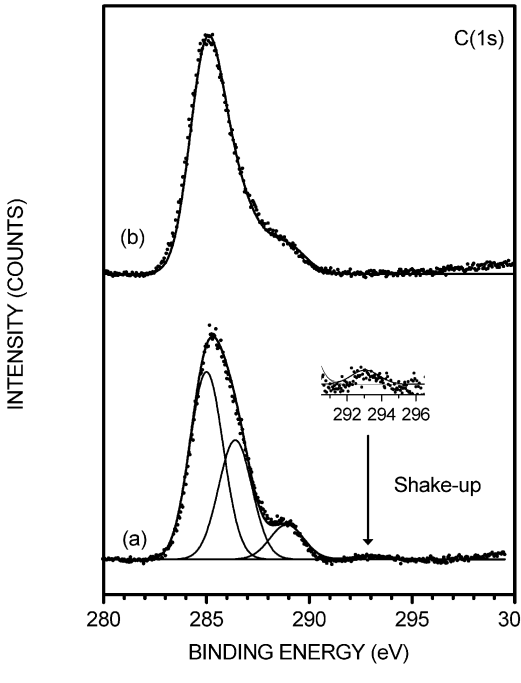

Fig. 1 C(1s) XPS spectra of furfuryl methacrylate plasma polymers deposited onto a flat glass slide: (a) pulsed (time on = 20 μs, time off = 20 ms, peak power = 40 W) and (b) 3 W continuous wave.

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b4/b412906g/
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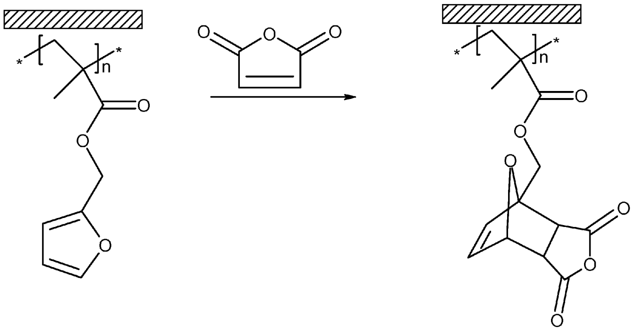
was attenuated, and also the π–π* shake-up satellite was absent, thereby reflecting greater fragmentation of the precursor under these harsher conditions.

Infrared analysis gave further evidence for high levels of structural retention during pulsed plasma polymerization, Fig. 2. First of all, the spectrum of the furfuryl methacrylate monomer could be assigned as follows:[25–27] 3122 cm^{-1} and 3152 (furan ring C–H stretching), 2900–2800 cm^{-1} (saturated C–H stretching), 1718 cm^{-1} (methacrylate C=O stretching), 1636 cm^{-1} (methacrylate C=C stretching), 1560 cm^{-1} and 1501 cm^{-1} (furan ring stretching), and 1013 cm^{-1} (furan ring breathing). There were also a variety of other fingerprint bands below 1000 cm^{-1}. The pulsed plasma polymer film exhibited all of these characteristic absorption features, except those associated with the methacrylate C=C double bond (*e.g.* 1636 cm^{-1} (methacrylate C=C stretching)). Also, the strong C=O stretch shifted to 1725 cm^{-1}, due to the loss of conjugation for the methacrylate carbonyl group following polymerization *via* its double bond (the weak shoulder at 1772 cm^{-1} can be attributed to other types of carbonyl environment formed under plasma polymerization conditions). Much broader absorption bands were measured for the continuous wave plasma polymer and the characteristic furan ring features were absent.

Following reaction of the furfuryl methacrylate pulsed plasma polymer layers with maleic anhydride, XPS elemental analysis indicated an increase in oxygen content, Table 1. This can be attributed to the incorporation of three additional oxygen atoms at the surface for each maleic anhydride molecule undergoing Diels–Alder chemistry with a furan ring, Scheme 1. The elemental stoichiometric ratio measured by XPS for this surface reaction is in good agreement with the predicted theoretical value, thereby implying that the extent of reaction is very high within the XPS sampling depth (*ca.* 2 nm), Table 1.

Grazing angle infrared spectroscopy of the Diels–Alder derivatized pulsed plasma polymer film indicated the presence of new peaks attributable to: anhydride C=O stretching (1860 cm^{-1}), C=C stretching (1636 cm^{-1}), and an intense broad band due to C–O–C ether stretching (1070 cm^{-1}), Fig. 3.[25] The Diels–Alder reaction also gave rise to an enhancement in the shoulder at 1772 cm^{-1} due to overlap with the maleic anhydride C=O stretching feature in this region. The overall predominance of the underlying pulsed plasma polymer film infrared absorption features following [4 + 2] cycloaddition chemistry with maleic anhydride is consistent with the reaction taking place at just the outer surface of the deposited layer (the sampling depths of grazing angle infrared spectroscopy and XPS being a few microns and *ca.* 2 nm respectively).



Scheme 1 Reaction of furfuryl methacrylate pulsed plasma polymer surface with maleic anhydride.

The aforementioned surface functionalization chemistry was found to be readily adaptable to a host of different materials and geometries. These include polymer microspheres, textiles, and metal tubes.

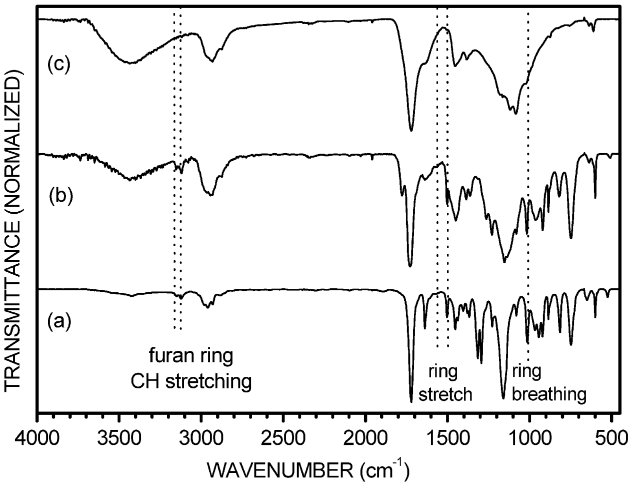


Fig. 2 Infrared spectra of (a) furfuryl methacrylate monomer; (b) pulsed plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W); and (c) 3 W continuous wave plasma polymer.

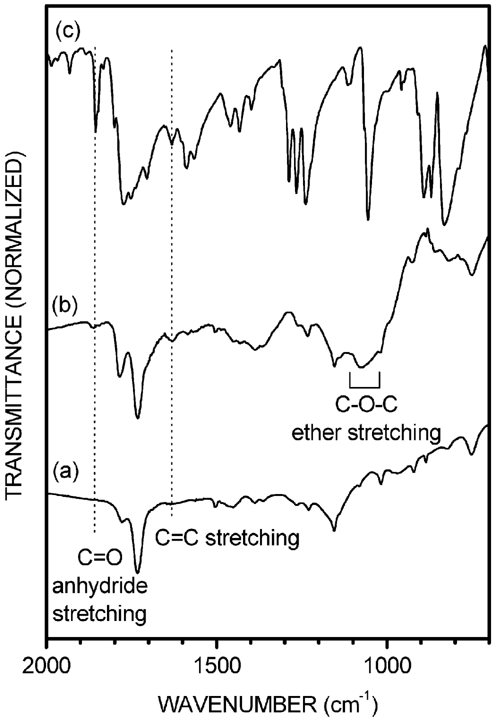


Fig. 3 Infrared spectra of (a) furfuryl methacrylate pulsed plasma polymer (grazing angle FTIR, time on = 20 μs, time off = 20 ms, peak power = 40 W); (b) furfuryl methacrylate pulsed plasma polymer reacted with maleic anhydride (grazing angle IR); and (c) maleic anhydride (diamond ATR accessory).

To conclude, the methacrylate C=C double bond in furfuryl methacrylate (together with the substrate) is activated during the short pulsed plasma duty cycle on-time followed by conventional polymerization proceeding within each associated extinction period. This yields furan functionalized surfaces which readily undergo the [4 + 2] Diels–Alder cycloaddition reaction with maleic anhydride. In contrast to all previous reported examples of surface Diels–Alder chemistry, this methodology is shown to be a mainly substrate-independent technique.

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