COVALENT ANCHORING OF POLYMER FILMS ON SILICON

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INTRODUCTION

Anodic decomposition of Grignard compounds RMgX at the hydrogenated surface of a silicon electrode leads to the formation of organic radicals able to abstract hydrogen atoms from the surface, leading to substitution of the hydrogen by organic groups covalently bound to silicon. The reaction is initiated by the formation of radical species $R^•$, which abstract a hydrogen atom from the Si surface, allowing for its substitution by a second $R^•$ radical. In the case of alkyl groups, the reaction is self-limited by steric hindrance between the grafted groups, so that typically 50% of the hydrogens can be substituted (nearly 100% for methyl) [1,2].

$$\equiv SiH + 2RMgX + 2h^+ \rightarrow \equiv SiR + RH + 2MgX^+.$$

If R is an organic group less inert than an alkyl, it may be expected that the Si surface coated with R groups will be as much reactive as the initial hydrogenated surface, hence leading to formation of a polymer layer. This possibility has been explored here.

EXPERIMENTAL

(111) p-Si surfaces were prepared atomically flat using oxidation and oxide stripping in deaerated ammonium fluoride. The state of the hydrogenated surface was checked by infrared (IR) spectroscopy in the multiple-total-internal-reflection geometry (sample size 15×15×0.5 mm^3, 45° bevels, 30 reflections at the surface). The Grignard electrolytes were 1M vinylmagnesium bromide in tetrahydrofuran, 3M phenylmagnesium bromide and 1M 4-chlorophenylmagnesium bromide in diethylether. Anodic modifications in the Grignard electrolytes were performed in a PTFE cell placed in a glove box, by applying a typical current of 0.1-1 mA/cm^2 with a copper counterelectrode. After modification, the samples were rinsed in anhydrous diethylether, then in bromobutane. After being taken out from the glove box, the surface was finally rinsed in ethanol and blown dry. The modified samples were characterised by IR spectroscopy and XPS. In-situ monitoring of the kinetics of modification was investigated using IR spectroscopy in a leak proof cell, the Si internal-reflection sample being pressed with a PTFCE-coated O-ring seal against an aperture in the cell wall.

RESULTS

In situ IR data confirm the loss of hydrogen after passing a few hundred $\mu C/cm^2$ through the interface. With increasing Faradaic charge, new absorption lines appear, characteristic of a growing polymer layer. Ex-situ IR and XPS spectra allow for identification of the polymer. Phenylmagnesium bromide leads to the formation of polyphenylene, which is clearly due to substitution of a hydrogen of the grafted layer by a phenyl group. A related polymer is formed for the case of 4-chlorophenylmagnesium bromide. However, significant amounts of chlorine appear to be incorporated into the film. This indicates that chlorine is not a preferred site for substitution. For the case of vinylmagnesium bromide, the substitution reaction should lead to formation of polyacetylene. However, in all the cases, the absorption in the region 2800-3000 cm^{-1} indicates that a significant amount of saturated aliphatic CH's is present in the layer. This is attributed to the presence of addition reactions, which lead to breaking a significant fraction of the double bonds.

Also, reaction of the radicals with the ether may lead to incorporation of fragments from the ether into the polymer. This incorporation depends on the solvent used, in the order toluene > tetrahydrofuran > diethylether > benzene. This sequence is just what one expects from the fragility of the solvent, the energy of the weakest CH bond increasing from toluene (85 kcal/mol) to the ethers (92 kcal/mol) and to benzene (111 kcal/mol). We have indeed checked that using benzene or 1,2-dichlorobenzene as the solvent allows one to obtain a better control of polymer composition.

CONCLUSION

Anodization of p-Si in suitable Grignard electrolytes appears as a flexible way to make polymer layers covalently anchored to the Si surface. Purity of the polymer is optimized by choosing a solvent resistant to radical attack. The method appears potentially usable for the formation of conducting as well as insulating polymer layers.

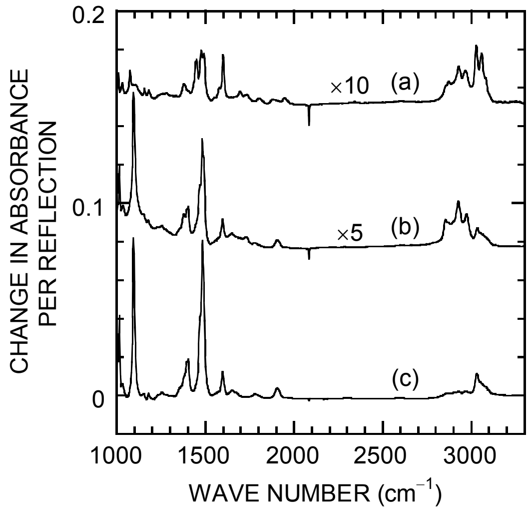

Fig. 1: Typical ex-situ IR spectra (absorbance referred to the initial hydrogenated surface: notice the sharp negative peak at 2080 cm^{-1}, associated with loss of the surface SiH bonds). (a) polyphenylene from $(C_6H_5)MgBr$ in diethylether, (b) polyphenylene from $Cl(C_6H_4)MgBr$ in diethylether, (c) same as (b) in benzene solvent. Notice the strong decrease of the saturated CH's (region 2800-3000 cm^{-1}).

REFERENCES

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