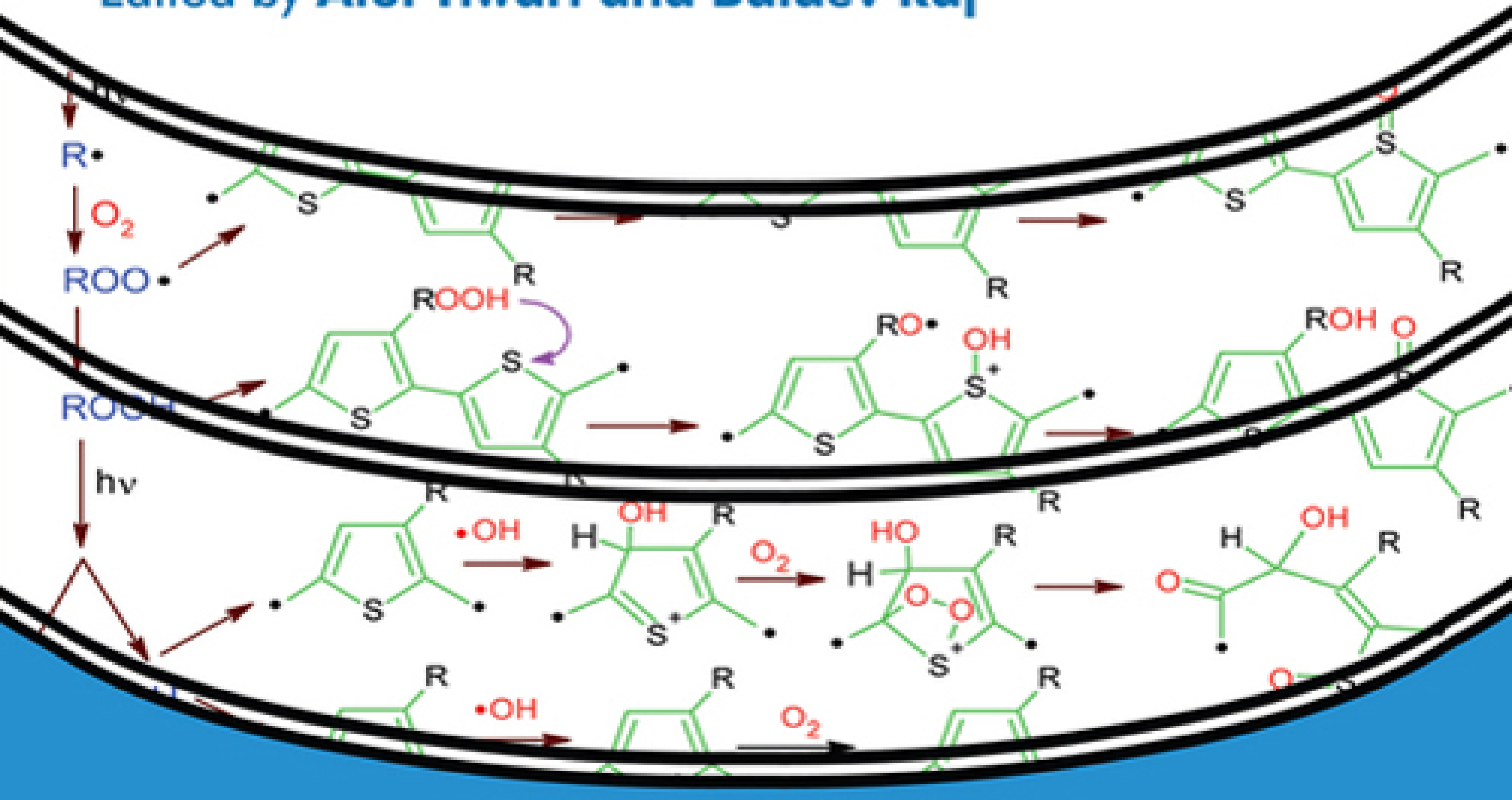
Materials Degradation and Failures Series

Reactions and Mechanisms in Thermal Analysis of Advanced Materials

Edited by **Atul Tiwari and Baldev Raj**



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Reactions and Mechanisms in Thermal Analysis of Advanced Materials

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Materials Degradation and Failure Series

Studies and investigations on materials failure are critical aspects of science and engineering. The failure analysis of existing materials and the development of new materials demands in-depth understanding of the concepts and principles involved in the deterioration of materials The *Material's Degradation and Failure* series encourages the publication of titles that are centered on understanding the failure in materials. Topics treating the kinetics and mechanism of degradation of materials is of particular interest. Similarly, characterization techniques that record macroscopic (e.g., tensile testing), microscopic (e.g., *in-situ* observation) and nanoscopic (e.g., nanoindentation) damages in materials will be of interest. Modeling studies that cover failure in materials will also be included in this series.

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Preface

Knowledge and experience relating to the stability of man-made materials is of great importance for realizing suitable and reliable technologies. Control over the physico-mechanical properties of a synthetic material can be achieved by selecting the proper chemical ingredients and reacting them under appropriate optimized conditions. High chemical, environmental, mechanical and thermal stability is often desired from a high-performance material. Knowledge of the thermal stability of a material as a function of time and temperature could provide valuable insights related to performance during the service life span of the material and, indeed, for life management too. High thermal stability is desired in materials operating in extreme service conditions, while moderate to low for biological applications.

Extensive amounts of published literature are available on the thermal analysis of materials. However, the content of most of the published papers is limited to monitoring of thermal degradation steps. It is extremely difficult to find articles on the mechanisms of decomposition of materials, partly because such studies are difficult to establish and justify. Several books are available on fundamental aspects of the techniques; however, application of these techniques to new materials has not yet been properly documented. We have noticed that researchers find it difficult to understand and explain the reasons behind the multiple-step decomposition patterns in their materials. The poor availability of understood investigations with good insights into the mechanistic routes and associated reactions has been the primary reason for such a lacuna. In this book, we have invited authors who have expertise in dealing with thermal analysis of materials and suggested that they contribute chapters focusing on the reactions occurring during thermal decomposition and mechanisms of reactions during such processes.

This edited volume consists of twenty-two chapters relating to the reactions and associated mechanisms observed in advanced materials as a function of time and temperature. It is divided into two parts; the first part containing information about degradation of polymeric materials and the second part devoted to materials other than polymers. The first chapter discusses thermal stability of organic layers grafted onto silicon and the reaction mechanisms of thermal degradation occurring in such hybrid systems. The use of thermogravimetric analysis to characterize biomedical ultrahigh molecular weight polyethylenes is discussed in a separate chapter, followed by a study on how thermal analysis controls the phase composition, size, and porosity of materials. Similarly, the reactions occurring in composites of high-density polyethylene containing magnesium hydroxide as flame retardant are presented in a committed chapter. Another chapter is devoted to the study of changes in thermal properties, crystallinity and decomposition kinetics during the degradation of aliphatic polyesters. A detailed investigation of polymer degradation modes and degradation mechanisms under thermal, chemical, biological, and radiation effects has also been provided as a separate chapter. Additionally, this chapter provides a fundamental overview of widely-accepted mechanisms and methods of applying these mechanisms, either individually or in combination with the existing high-end polymers. Thermal degradation of polyurethanes is covered in another chapter, and several techniques to study the degradation processes, degradation mechanisms, and ways for improving their thermal stability are highlighted in a chapter related to polyurethanes. Likewise, the design, degradation behavior, associated mechanisms, and structure-property relationship of thermally reworkable epoxy resins have been added in a separate chapter.

The degradation pattern and mechanism of thermal decomposition of vinylidene chloride polymers have been systematically described in a separate chapter, followed by an overview chapter on the use of mass spectrometry as an analytical tool to investigate the thermal degradation mechanisms in macromolecules. Another important study on the degradation behavior of general purpose poly(styrene) has been carefully described in a separate chapter. The reaction mechanisms involving the degradation of lipid-based compounds such as Brazil nut oil have been explored in an individual chapter, followed by a study on the reaction mechanism during thermal degradation of cellulose and cellulosic substrates such as cotton and paper.

An interesting study reporting on sodium alkoxides under isothermal and non-isothermal conditions using the thermogravimetric method has its own chapter, followed by a chapter on the influences of temperature on the products obtained through thermal processing of hard tissues. A unique chapter on the application of the hydrothermal method for the treatment of waste electric and electronic equipment has also been included. Another chapter describes the theoretical criteria for carrying out the evaluation of a masonry structure affected by high temperature firing. It is evident that the heat processing step produces molecular changes in muscle proteins that affect the functional and textural properties, resulting in the alteration of the quality of the final product. A chapter highlights the use of spectroscopic techniques in determining the protein structural changes in muscle food products and blood plasma during heating. The effect of temperature on the structural and textural properties of layered double hydroxide-based catalyst has also been postulated on, followed by a study to evaluate the degradation process of ten different natural fibers by X-ray diffraction and thermogravimetry techniques. The kinetic mechanism for non-isothermal degradation of solids has been described in the final chapter.

We are confident that after reading these chapters, students and researchers will develop a deeper understanding of the degradation patterns in advanced next-generation materials and could devise the mechanistic routes of decomposition in their materials based on robust insights. Such contributions by the readers could further push the frontiers of the science and technology of degradations, a vital pursuit. This is a useful book for readers from diverse backgrounds in chemistry, physics, biology, materials science and engineering, including chemical engineering. This book can be used as a reference for students and research scholars and as a guide for technologists working in the industry.

Atul Tiwari, PhD
Baldev Raj, PhD
June 1, 2015

Part 1

DEGRADATION OF POLYMERS

Chapter 1

Thermal Stability of Organic Monolayers Covalently Grafted on Silicon Surfaces

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Abstract

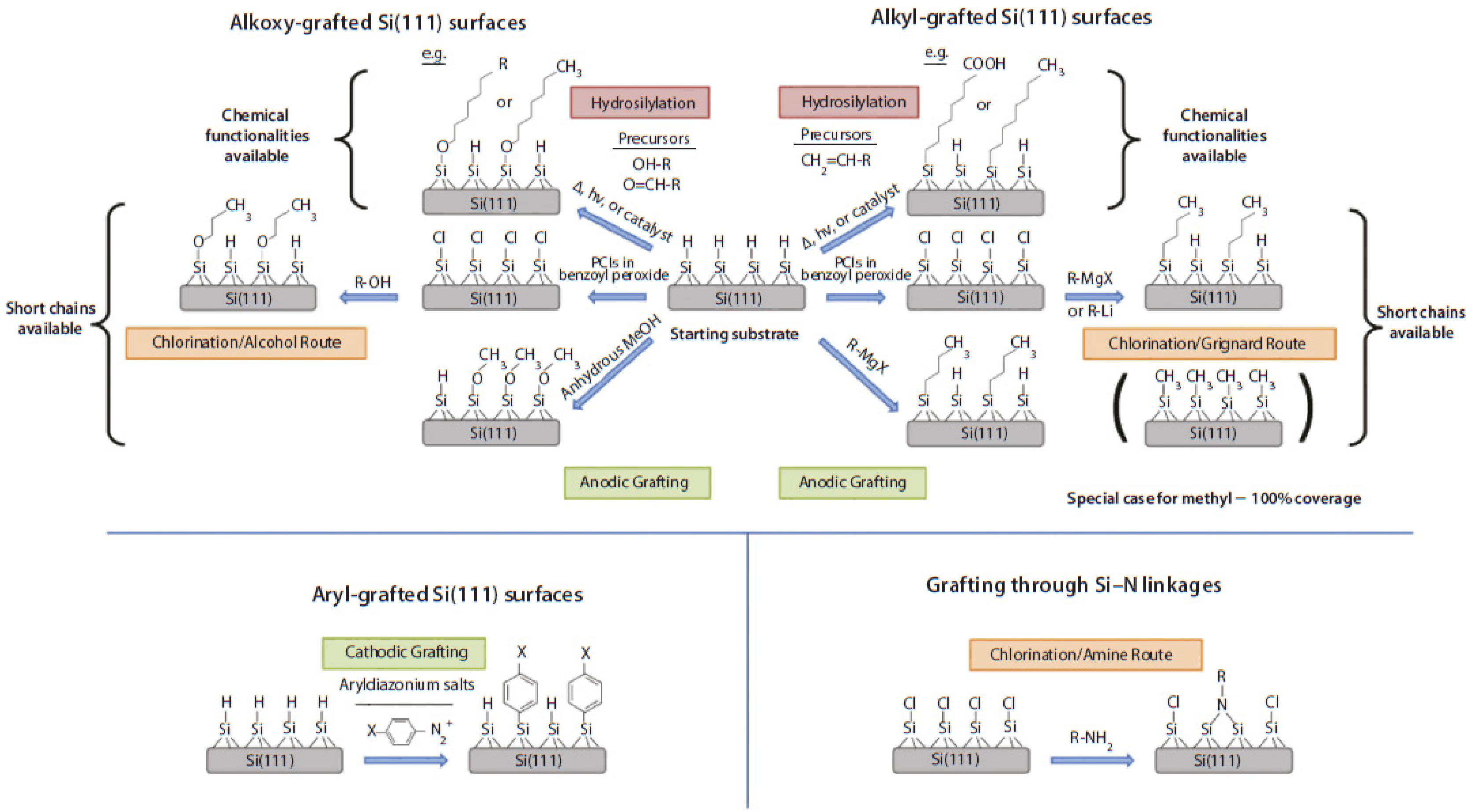
Organic modification of silicon surfaces is a topic of high interest in fundamental surface chemistry research as well as for the development of technological applications ranging from microelectronics to photovoltaics and biotechnology. Over the past decades, many approaches to anchor covalently organic monolayers to hydrogen-terminated silicon surfaces have been investigated. These organic monolayers may bear specific terminal groups depending on the application aimed at. Also, they may be used as buffer layers to protect the silicon surface against oxidation in contact with atmospheric environment or aqueous media. In the context of further modification of the silicon surfaces (e.g., in microelectronics), thermal processes at temperatures higher than ambient are necessary; thus, the understanding of the reaction mechanisms of the thermal decomposition of such organic layers may become an important issue. In this chapter, the thermal stability of organic layers grafted onto silicon surfaces is reviewed, and the reaction mechanisms of the thermal degradation occurring on these hybrid systems are discussed.

Keywords: Thermal stability, silicon, organic modification, grafting, organic monolayers, alkyl/alkoxy chains, aryl groups, Si–N linkages, heterostructures, silicon hybrid systems, reaction mechanisms

1.1 Introduction

Organic modification of semiconductor materials [1–5], especially silicon (Si) [1, 2, 5], has attracted increasing interest because of the importance of understanding, controlling, and tailoring the properties of these organic/inorganic interfaces. Nowadays, the importance of surface chemistry in fundamental research and technological applications has grown up together with the ability to selectively modify *oxide-free* Si surfaces. Functionalization of Si surfaces by grafting organic molecules onto the hydrogen-terminated Si surface, which leads to the formation of covalent Si–C, Si–O–C, or Si–N bonding, opens the way to various applications ranging from molecular electronics [6–8], microelectronics [9–13], and photovoltaics [14–18] to photoelectrochemical devices [19, 20]. Two different pathways can be used to tether organic species on Si surfaces. One is to start from clean and reconstructed Si surfaces in ultrahigh vacuum (UHV) conditions (e.g., by heating the sample up to 1000 °C), which can subsequently react with organic compounds in UHV [3, 5, 21, 22]. Another pathway, which will be our main focus, consists in reacting an H- or Cl-terminated Si surface with organic functions at ambient pressure using suitable precursor molecules. The processes are often conducted by dissolving the precursor in an organic solvent or with the neat liquid. Figure 1.1 summarizes the main methods to covalently anchor organic molecules to *oxide-free* Si surfaces by wet chemical means. The formation of well-ordered organic monolayers covalently bonded to Si using the latter process has been the subject of many studies. Among those are studies on alkyl [23–33], alkenyl [34–38], alkynyl [38–43], and alkoxy chains [44–54], aryl groups [55–67], and chains bearing a functional termination [68–73] to name a few. Moreover, the presence of functional groups, such as –OH, –COOH, or –N_3, on top of the grafted organic monolayer, may be a starting point to extend the library of available chemical terminal groups, in particular to develop Si-based chemical and biochemical sensors [74–78], e.g., using click chemistry [79–83]. The organic/Si hybrid system can be achieved via a wide variety of wet chemical [84], photochemical [85], and electrochemical [86] methods. Among the wet chemical methods, the hydrosilylation route [87, 88], which is a well-known reaction in organic chemistry, is widely used to make alkenes, alkynes, or other unsaturated hydrocarbon compounds react with a H-terminated Si surface. Electrochemical grafting can be made from organolithium or Grignard reagents [26, 40, 89] in anodic conditions, or from diazonium compounds in cathodic conditions to obtain aryl-grafted surfaces [55, 90–92]. Among these methods, those which have been used in connection with thermal stability studies will be briefly described in the corresponding subchapters. However, since a thorough description of these organic grafting methods is beyond the scope of this chapter, we suggest the interested reader to refer to the several excellent reviews on this topic already published over the past decades [1, 2, 84, 93–95]. The different approaches to form *oxide-free* organic/Si-based hybrid interfaces presented in this chapter are summarized in Figure 1.1, in the case of H-terminated Si(111) surfaces, but can also be extended to other types of Si surfaces. Organically modified Si surfaces exhibit excellent electronic quality (low concentration of surface states in the mid-gap) and improved chemical resistance against the formation of an oxide layer under exposure to ambient air [27, 90, 96–99] or in aqueous media [100–104].

Figure 1.1 Schematic illustration of the different chemical modification pathways to obtain organically modified Si surfaces from atomically flat H-terminated Si(111) surfaces as starting substrates.


Alkoxy-grafted Si(111) surfaces
Alkyl-grafted Si(111) surfaces
Chemical functionalities available
Chemical functionalities available
e.g.
or
Hydrosilylation
Hydrosilylation
Precursors
OH-R
O=CH-R
Precursors
CH2=CH-R
Δ, hν, or catalyst
Δ, hν, or catalyst
PCl5 in benzoyl peroxide
PCl5 in benzoyl peroxide
Starting substrate
Anhydrous MeOH
R-MgX
R-OH
R-MgX or R-Li
Short chains available
Short chains available
Chlorination/Alcohol Route
Chlorination/Grignard Route
Anodic Grafting
Anodic Grafting
Special case for methyl – 100% coverage
Si(111)
Aryl-grafted Si(111) surfaces
Cathodic Grafting
Aryldiazonium salts
Grafting through Si–N linkages
Chlorination/Amine Route
R-NH2

Thermal stability of the grafted organic monolayers may also become an issue in the context of microelectronics because there is an increasing need to replace the silicon dioxide (SiO_2) gate insulator in the elementary metal-oxide-semiconductor field-effect transistors (MOSFETs) by a material with a higher dielectric constant (so-called “high-κ oxide”, e.g., HfO_2, whose dielectric constant is 4–6 times as high as that of SiO_2) [105–107]. The replacement of the SiO_2 gate oxide layer is necessary to keep the switching performances of individual MOSFETs and to reduce the leakage current appearing upon decreasing the size of the elementary MOSFETs [108–110]. However, the deposition of high-κ oxides on silicon substrates is accompanied with the formation of an SiO_2 interlayer and/or silicate between the silicon and the high-κ oxide, leading to an unwanted series capacitance [111]. In this context, the passivation of the silicon surface with an ultrathin organic layer such as a short alkyl or alkoxy layer [13], or by the formation of Si–N linkages [112] was proposed to reduce SiO_2 formation. For instance, oxygen diffusion was retarded by depositing HfO_2 on a nitride-passivated Si surface, which minimized the formation of interfacial SiO_2 compared to the case of HfO_2 grown on an H-terminated Si surface [113]. In many instances, the deposition of the high-κ oxide is performed at temperatures well above 300 K, and post-annealing treatments may be necessary to remove organic contaminations and/or cure out defects in the as-deposited oxide. This raises the question of the thermal stability of the organic layers, which is the key issue. The reaction mechanisms of the thermal decomposition of these organic layers will be described in this chapter.

For good electronic properties of the grafted Si surface, an obvious prerequisite is that the starting surface (H-terminated Si surface) has to be as clean as possible, presenting a high degree of passivation without defects.

1.1.1 Hydrogen-Terminated Si Surfaces

Obtaining an H-terminated Si surface is easily achieved at ambient by selective etching of the native oxide in aqueous fluoride solutions or even in alkaline solutions where Si is etched at a high rate [114–117]. This surface chemistry, also theoretically explained by ab initio calculations [118], confers this surface unique properties. It is quite hydrophobic (contact angle ~90 °), stable in air, and it takes several hours to grow a native oxide layer. From an electronic viewpoint, H-terminated Si surfaces are known to present the slowest recombination velocity ever reported due to the absence of any surface states in the band gap [119]. From a structural viewpoint, Si etching becomes more and more anisotropic with increasing pH. In alkaline solutions [120, 121] and in 40% NH_4F [122], the (111) planes are etching stop planes for steric reasons while the (100) and (110) planes undergo faster dissolution. At low pH, the overall etching is quasi isotropic.

Obtaining an H-terminated Si(111) model surface with 100 nm wide terraces (miscut 0.2 °) free of etch pits and separated by rectilinear atomic steps, such as the one in Figure 1.2a, is feasible because this plane is an etch-stop plane. This requires, however, careful operating conditions. The NH_4F solution must be oxygen-free [123], by bubbling it with N_2 or adding sulfite ions as an oxygen scavenger [124], the sample must present a rough part to act as sacrificial anode [117, 125] and the miscut must be precisely aligned toward the $[11\bar{2}]$ direction [117, 125]. On the atomic scale the terraces present a (1 × 1) structure (see inset of Figure 1.2a) with $7.8\ 10^{14}$ vertical monohydride (≡Si–H) sites per cm^2 in agreement with the narrow IR band at 2083 cm^{-1} observed in p-polarization only (see Figure 1.2b). If one of these conditions is not fulfilled, a larger density of structural defects, associated with dihydride ($=SiH_2$) sites, is observed (these are located at triangular etch