57.1 INTRODUCTION

The explosive growth of semiconductor industry has been fueled by the relentless pursuit for miniaturization of semiconductor devices. The minimal feature sizes or critical dimensions (CDs) of semiconductor devices in mass production have shrunk from 10\(\mu\)m more than 30 years ago to less than 100 nm in 2005. According to the International Technology Roadmap for Semiconductors, this miniaturization trend is expected to continue unabated with the production of sub-25 nm generations of devices later next decade [1]. The miniaturization of semiconductor devices has made it possible to offer a host of sophisticated devices and equipment, from super computers, personal computers, personal digital assistants, cellular phones to medical devices and household appliances, with ever increasing performance at steadily reduced prices per transistor or bit.

This miniaturization trend has been made possible by advances in a critical device patterning process called photolithography, including constantly improved photosensitive polymeric materials called photoresists, advances in optical lenses, and the use of shorter wavelengths of light for patterning. In 2004, the semiconductor industry quietly ushered in the Nanoelectronics Age with the mass production of sub-100 nm node devices. The current leading-edge semiconductor devices in mass production—the so called 90 nm node devices—have a transistor gate length of less than 50 nm. These leading-edge devices are fabricated using photoresists based on alicyclic polymers at 193 nm wavelength, as well as Novolak-based mid-ultra violet (MUV) photoresists or poly(4-hydroxystyrene)-based deep UV (DUV) photoresists at wavelengths of 365 and 248 nm, respectively.

57.2 PHOTORESIST MATERIALS AND LITHOGRAPHIC PATTERNING PROCESS

In a typical photolithography process, a UV light is projected by a set of sophisticated lenses onto a silicon wafer coated with a thin layer of photoresist through a mask that defines a particular circuitry. Exposure to the UV light, coupled with a subsequent baking, induces photochemical reactions that change the solubility of the exposed regions of the photoresist film. Subsequently an appropriate developer, usually an aqueous base solution, is used to selectively remove the photoresist either in the exposed regions (positive-tone photoresists) or in the unexposed regions (negative-tone photoresists). The pattern thus defined is then imprinted on the wafer by etching away the regions that are not protected by the photoresist with reactive ion (plasma) etching (RIE). Figures 57.1 and 57.2 depict schematic of a typical photolithographic system and a typical device patterning process. Excellent reviews on photoresist materials have been published [2–6].

Advanced photoresists, such as 193 and 248 nm photoresists, are based on chemical amplification concept [7,8]. These chemically amplified photoresists generally consist of a base polymer, a photo-sensitive compound called photoacid generator (PAG), and sometimes a cross-linking
agent for negative-tone photoresists. When these resists are exposed to UV irradiation, a strong acid is generated in the exposed regions as a result of the photochemistry of the PAG. This strong catalytic acid then induces a cascade of subsequent chemical transformations of the photoresist that alter the solubility of the exposed regions. Thus the quantum efficiency of the photochemistry is amplified by hundreds or even thousands of times through the catalytic chain reactions. This catalytic effects of the chemical amplified resists greatly enhance the sensitivity of a photoresist, thus the efficiency of photolithographic processes. The chemical amplification process of a positive-tone resist is illustrated in Scheme 57.1. The most popular chemical amplification involves the acid catalyzed deprotection poly(4-hydroxy-styrene) or poly(acrylic acid) protected by various acid sensitive protecting groups for positive-tone photoresists using a photoacid generator (PAG) [9].

The key figures of merit for a photoresist are resolution, process latitudes (dose and focus), and reactive ion etch resistance. Other important performance parameters include sensitivity, compatibility with industrial standard developer (0.263N aqueous tetramethylammoniumhydroxide (TMAH) solution), adhesion to substrates, environmental stability, and shelf life. These performance characteristics are mainly determined by the base polymer in the photoresist. It should be pointed out, however, that some of these performance parameters, such as resolution, process latitudes and etch resistance, are also tool and process condition dependent.

Polymers for advanced photoresists, therefore, need to meet the following requirements in order to deliver the performance necessary for device fabrication: good transparency at the imaging wavelength, etch resistance, optimal dissolution properties, high sensitivity, compatibility with the industrial standard 0.263N TMAH developer, as well as thermal and mechanical properties and shelf life requirements. These stringent requirements led to the design and synthesis of distinct polymer platforms for the evolving lithographic exposure technologies. Table 57.1 summarizes the major polymer platforms for the various exposure technologies.

Photoresists can be classified into three categories based on the lithographic processes: single layer photoresists (SLRs), bilayer photoresists (BLRs), and top surface imaged (TSI) photoresists [5]. Single layer photoresists have traditionally been the work horse for patterning semiconductor devices due to its process simplicity as compared with the bilayer and the TSI processes.

Properties of photoresist polymers were surveyed and reviewed by Kunz [10]. This present chapter is intended to complement, not replace, the review chapter by Kunz. Emphasis in this chapter has been placed on physical property data of photoresist polymers published after Kunz’s review.